INVESTIGATIONS IN MOTHPROOFING, WITH SPECIAL REFERENCE TO THE USE OF SYNTHETIC ORGANIC COMPOUNDS

BY

CARL JOHN WEINMAN

B.A., University of Illinois, 1936
M.A., University of Minnesota, 1937

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN ENTOMOLOGY IN THE GRADUATE SCHOOL OF THE UNIVERSITY OF ILLINOIS, 1940

URBANA, ILLINOIS

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I. Introduction

These investigations were begun as a study of mothproofing agents now in use, with the special purpose of finding one suitable for the mothproofing of the felt parts of pianos. When early experimentation indicated that there is not at present a commercial mothproofing material entirely adequate for the purpose, the writer undertook to investigate the various synthetic organic compounds.

The materials were tested with the thought in mind that a good, general, household mothproofing preparation should conform to all of the following qualificatins:

1. Highly toxic to the destructive stages of all fabric insects
2. Effective for a period of at least one year
3. Non-corrosive to metals
4. Non-staining
5. Non-irritating to the user at the time of application and thereafter
6. Not detrimental to highly polished wood surfaces
7. Having the lowest practical surface tension (for maximum penetration)
8. Having no deleterious effect on wool fibers
9. Reasonable in price

II. Acknowledgment.

The writer expresses his appreciation to Dr. C. L. Metcalf, who suggested the problem and directed the work, and to Dr. W. P. Hayes, Prof. W. P. Flint, Dr. C. W. Kearns, Dr. L. P. Kyrides, and Mr. H. L. Morrill for various valuable services.

III. Literature

Although almost every imaginable material, from ordinary pepper to the most complicated of organic and inorganic chemicals, has been proposed as a remedy for the $100,000,000 to $250,000,000 loss of property estimated to be damaged annually by fabric pests in the United States, only the use of various silicofluorides in water and of a solution of cinchona alkaloid in oil are indicated in the literature as being widely accepted as household, mothproofing agents. Most of the scientific research

in the field of mothproofing has been done during the past twenty years, with the result that there still are large numbers of products advocated for home use. By far the most commonly used of these are solutions of toxic inorganic salts in water solutions.

IV. The Important Fabric Insects in the United States

Nearly all of the damage to fibers of animal origin can be traced to members of one or the other of two groups of insects: the clothes moths (order Lepidoptera, family Tineidae) and the carpet beetles (order Coleoptera, family Dermestidae).

Among the clothes moths, three species, the webbing clothes moth (*Tineola biselliella* Hummell), the case-making clothes moth (*Tinea pellionella* Linné), and the tapestry clothes moth (*Trichophaga tapetzella* Linné) are of special importance. All of these moths lay large numbers of eggs, from which hatch tiny, white caterpillars, the destructive form of the insects. Under favorable conditions, these insects may have three or four generations a year.

Several species of carpet beetles, belonging to two genera, are very important fabric pests, although they feed on a great variety of animal and cereal products. The black carpet beetle, *Attagenus piceus* Olivier is the most important and most widely distributed, but the common carpet beetle or "buffalo moth", *Anthrenus scrophulariae* Linné and the varied carpet beetle, *Anthrenus verbasci* (Linné) are generally distributed throughout the country. The furniture carpet beetle, *Anthrenus vorax* Waterhouse, introduced into the United States in 1911, is a serious pest only in the eastern section at the present time.

As with the clothes moths, only the larvae of carpet beetles feed on fabrics, but, unlike the clothes-moth larvae, they require about a year to complete their development. Some individuals, usually because of a scarcity of good food but sometimes for no apparent reason, require as long as three years to complete their life cycle.

V. Methods

Recently there has been considerable agitation for the adoption of a standard method of testing treated wool for resistance to attack by fabric pests. Although the adoption of such a stand-

ard might be desirable, the difficulties of securing the approval of a method by chemists, entomologists, and textile workers are enormous. There exists also the very real possibility that differences in techniques must be made to accommodate the differences in types of mothproofing agents being tested. Nevertheless, it becomes of greatest importance for a worker to justify fully his choice of methods.

Although it is clearly necessary to test a mothproofing material against both clothes moths and carpet beetles before one can claim the material to be adequate, it is not at all necessary to use more than one species of insect in preliminary tests, for the obvious reason that if the material is not proof against one species, it definitely is not mothproof. It follows that much time can be saved by using the hardiest, most voracious, and most resistant species for all preliminary tests.

Larvae of the black carpet beetle, *Attagenus piceus,* were used for all preliminary experiments in these investigations. This insect has been generally recognized as being much more hardy and resistant than any of the clothes moths, and it is the most important species of carpet beetle economically. Moreover, it is readily available in large numbers and requires no special caution in handling or rearing. The larvae will feed voraciously on pure wool and can even complete their development on this material.

The type of solvent to be used as a carrier for the toxic agent usually depends on the nature of that toxic agent, inasmuch as few compounds are readily soluble in both water and organic solvents. In these studies, however, those materials which are suitable for use in organic solvents have been given the greatest consideration. The chief reason for this is that water, even with a wetting agent, has more than twice as great a surface tension as the petroleum oils commonly used as carriers for organic insecticides. This means, of course, that it is impossible to get effective penetration with a water-base spray, unless the material being treated is actually soaked with the mothproofing solution. But if this is done, the water itself is very likely to injure the finish of the fabric.

It is true, of course, that water is the cheapest base material that can be used, but the disadvantages of its use, such as poor

penetration, shrinking of woolens, spotting of varnished surfaces and silk linings of woolen clothes, and its lack of larvacidal action, make it a poor bargain, when suitable petroleum oils can be purchased for as little as twelve cents per gallon.

Only pure wool, white flannel was used in these investigations. White wool was chosen so that no complications from the presence of a dye could be used. The wool was cut into circles, three and one-half inches in diameter, and these were treated by immersion in the mothproofing solution. After the circles had been completely saturated, they were transferred to a clean, dry screen and left there until the solvent had evaporated. Before being infested, the test circles were cut in half, and the resulting two semi-circles were fastened at one end by means of a brass clip. The chief reason for using semi-circles of two thicknesses instead of a whole circle of only one thickness is that the larvae of both clothes moths and carpet beetles seem to prefer to feed between two surfaces. The use of semicircles also provides a convenient method of comparing two different treatments in the same dish.

Ten carpet-beetle larvae of various sizes (except that no very small ones were included) were used on each test. This concentration is equivalent to about one larva per square inch of wool. Whenever a treatment killed these first larvae and prevented feeding, ten more larvae were placed on the same test circle, and the wool was similarly reinfested so long as it resisted damage.

Ordinarily, the larvae were not given a choice of food; i.e. they had to eat the treated wool or starve. Whenever untreated check wool was placed adjacent to the treatment in the same dish, the larvae always preferred to feed on the check wool, except in instances where the treatment consisted of inorganic toxicants applied in water. When it was discovered that wool treated with the oil solvent alone was repellent compared with untreated or water-treated wool, it became clear that repellency is only a matter of degree, and that there was little to gain by placing a check treatment adjacent to a mothproofed treatment.

In all of the experiments conducted in this study, the treated wool was placed in open petri dishes, and these were left uncovered throughout the tests. This procedure provides for the

escape of any vapors which might be given off from the treated wool and which might have a fumigating effect on the larvae, if the vapors were confined. Covering the dishes would also prolong the effectiveness of a volatile mothproofing agent, by preventing the escape of the toxicant through evaporation and diffusion.

In an attempt to speed up the evaluation of apparently effective treatments, treated circles were subjected to heat, by means of placing them in an oven at a temperature of 60° Centigrade. (The choice of this particular temprerature was purely arbitrary.) By varying the concentration of toxicant in treating the wool, and by leaving the wool in the oven for varying periods of time, it was possible to get a comparison in stability of various compounds in a very short time. By this means, information which otherwise would not have been revealed until after a year or more of ordinary testing, was secured in the space of a few weeks.

VI. Experimental Results and Conclusions

Of all the commercial mothproofing preparations tested, only "Konate", an oil solution of cinchona alkaloid, approaches the qualifications stated in the introduction of this paper. Even this material falls short, however, in that it tends to stain white wool when heavily applied and in having little or no residual toxicity, although it does remain highly repellent. This product also is rather expensive.

The silicofluorides and other inorganic salts applied in water solution were effective in that they killed the larvae before very much damage had been done to the wool. These materials are not at all repellent, so that fabric insects feed on them readily until they consume a toxic dose of the salt. The use of such inorganic compounds is subject to the limitations common to all materials applied in water solutions.

The first of the synthetic organic materials tested was N,N-amyl-benzyl cyclohexylamine. This compound had previously been found by other workers to be the most promising of seventy-nine cyclohexylamine derivatives tested against the onion thrips, *Thrips tabaci* Lind., and the greenhouse red spider, *Tetranychus telarius* (Linné). Although N,N-amyl-benzyl cyclohexylamine was an effective mothproofer when first applied, it

was too volatile. A ten per cent treatment in oil lost its effectiveness after a seven-month exposure to light and air (at room temperature).

Other cyclohexylamine derivatives, as well as representatives of other classes of organic compounds, were tested in these studies. Actually, the following types of materials were tested: three primary monoamines, eleven secondary monoamines, five tertiary monoamines, ten polyamines, thirteen acylated amines (including both mono- and polyamines), sixteen chlorinated phenol compounds, nineteen heterocyclic compounds with N or N,N′ in a six-membered ring, and thirty miscellaneous materials, besides fourteen commercial preparations. In addition, experiments were conducted on several combinations of these compounds.

A number of the synthetic organic compounds show much promise of fulfilling the need for a really adequate toxicant for use in organic solvents. Some of the amines are very toxic to both clothes moths and carpet beetles, and nearly all of them are highly repellent. Unfortunately some of the most effective members of this class stain white wool rather severely, especially where the wool is in contact with metals. The staining can be corrected by forming acid salts of the amines or by converting them to amides through acylation. Either of these remedies, however, results in a great decrease in effectiveness.

Several of the chlorinated phenol derivatives are rather powerful stomach poisons, though they lack a very high degree of repellency. A few of the heterocyclic, nitrogen-containing compounds combine a high toxicity with strong repellency. Here again, however, the most effective compounds stain the wool seriously.

In attempting to correlate toxicity with molecular structure, it soon becomes apparent that, except within certain narrow limits, no close relationship exists. In general, however, there does seem to be a correlation between toxicity and molecular weight of the compounds. This relationship, although it is not valid for all the compounds tested, does, nevertheless, appear throughout the large groups to which the varying materials have been referred.

Vita

Born in Middletown, Ohio on March 27, 1915, Carl John Weinman attended the public schools of that city prior to his entering the University of Illinois in the fall of 1932. He was graduated with high honors in February, 1936, receiving the degree of Bachelor of Arts in entomology. After completing one semester and one summer school of work in the graduate school of the University of Illinois, he transferred to the University of Minnesota in the fall of 1936, having been the recipient of the Shelvin Memorial Fellowship for graduate study in that institution. He received the degree of Master of Arts in entomology in June, 1937.

The candidate returned to Urbana, Illinois, in June, 1937, to accept the position of assistant entomologist with the Illinois State Natural History Survey, with which organization he had been affiliated as a general assistant for three years prior to his going to Minnesota. He reentered the graduate school of the University of Illinois the following September, to continue work leading to the degree of Doctor of Philisophy in entomology.

From May to November, 1938, and again from April to October in 1939, the candidate was on leave of absence from the Illinois State Natural History Survey to work as state supervisor of grasshopper control for the United States Department of Agriculture, Bureau of Entomology and Plant Quarantine. He resigned this position as well as his position as assistant entomologist with the Natural History Survey in October, 1939, to become research assistant on an insecticide project sponsored by the Monsanto Chemical Company of St. Louis, Missouri. This project is established as a fellowship with the Illinois State Natural History Survey and the Illinois Agricultural Experiment Station.

The candidate is a member of Phi Beta Kappa, Phi Kappa Phi, and Sigma Xi honor societies.